Theoretical Analysis of the Methodology for Determining the Physicochemical Properties and the Experimental Results of Zeolites

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Abstract: Adsorption processes utilizing synthetic zeolites are extensively applied for the dehydration and purification of natural gas, owing to their high selectivity. Adsorptive drying enables the removal of moisture, hydrogen sulfide, hydrocarbons, and other contaminants that can negatively impact the efficiency of technological operations. Zeolites act as molecular sieves. This paper examines methods for determining the physicochemical and adsorption properties of zeolites employed in the desulfurization and drying of natural gas. A review of the literature indicates that the regeneration of molecular sieve adsorbents (zeolites) used for sulfur compound removal and the identification of their optimal applications remain highly relevant topics. Based on both literature data and experimental investigations, methodologies for assessing coke content, mechanical strength, specific surface area, porosity, and adsorption capacity of zeolites are described. The results of tests on regenerated zeolites with varying particle sizes are presented, along with comparative analyses relative to the original samples.

**Keywords:** zeolite, adsorption, regeneration, physicochemical characteristics, porosity, mechanical strength, bulk density, water absorption.

# INTRODUCTION

During extraction, natural gas removes moisture in its composition, which forms crystallohydrates with gas molecules at low temperatures. In the presence of water, corrosion processes of equipment intensify, and emergencies may occur due to blockage of gas pipelines and equipment of gas processing plants with hydrates. In this regard, the removal of moisture from natural gas is one of the necessary processes for preparing gas for transportation and further processing. The moisture content of the gas is determined by the dew point temperature and is regulated by acceptable standards (industry standards). The process of drying natural gases is an important and indispensable link in the process of their preparation for transportation via main gas pipelines [1-4].

Adsorption processes using synthetic zeolites are widely employed for the dehydration and purification of natural gas due to their high selectivity. Zeolites function as molecular sieves. Their extensive application is explained by the fact that they can separate substances not only through adsorption selectivity but also based on differences in the size and shape of the absorbed molecules. To penetrate the adsorption cavity, the critical diameter of the adsorbate molecule must be smaller than the pore opening of the zeolite.

Among the available purification methods, adsorption treatment is considered the most efficient approach for removing H2S, CO2, and NOx from natural gas. Gas purification using zeolites has become widespread because of several advantages, including high environmental efficiency, deep dehydration capacity, low specific adsorbent consumption, and favorable operational performance of adsorption units [1, 2].

According to the reviewed literature, zeolites used for desulfurization and dehydration of natural gas must possess a combination of strength, structural, and surface characteristics that meet industrial application requirements. The determination of these parameters is generally carried out following standards and sectoral guidelines. However, when developing zeolite regeneration technologies and evaluating their adsorption properties, additional analytical methods, laboratory tests, and pilot-scale experiments are also employed to obtain a more comprehensive understanding of the mechanisms governing adsorption activity formation [5-9.

# MATERIALS AND METHODS

To purify natural gas from mercaptans in the gas industry, the most effective adsorbent for drying gas is CaA zeolite to absorb carbon dioxide from the gas stream. Zeolite-containing rocks were used as a natural adsorbent and experiments using a synthetic CaA zeolite were also carried for comparison. As is known, zeolites used in adsorption cycles of desulfurization of natural gases, in addition to the main pores enclosed in the cavities of crystal lattices, have so-called transport pores (capillaries), which play an important role in adsorption processes. The main methods of natural gas drying are processes carried out by cooling, absorption and adsorption. Physico-chemical method of the process drying of natural gas, based on the absorption of moisture by various absorbers. In adsorption methods for drying gases, zeolites (natural or synthetic) are most used. To study the adsorption activity of samples of adsorbents for drying natural gas, we investigated:

* the method of determining the quantitative content of coke;
* the method of determining the strength of crushing granules;
* the method of determining the coefficient of abrasion resistance;
* the method for determining the total volume of pores by water absorption.

1. The carbon (coke) content is determined by a combustion-based analytical technique. This method relies on the complete oxidation of coke deposits, followed by the collection of combustion products — namely water vapor and carbon dioxide. The burning process is carried out in an air stream at a temperature range of 750–800 °C. To ensure full oxidation of carbon monoxide to carbon dioxide, the combustion gases are passed through a copper oxide tube heated to 350–400 °C.

CuO + CO CO2 + Cu

2Cu + O2  2CuO

Water vapor is captured using phosphorus anhydride (or silica gel), while carbon dioxide is absorbed by Ascarite. The increase in the mass of the Ascarite tube is used to determine the amount of coke deposited on the catalyst.

The coke content X (%) is calculated according to the following formula:

Х = =

*where: C1 – mass gain of the Ascarite tube, g; C2 – mass of the zeolite sample under investigation, g; 0.273 – conversion coefficient used to calculate the carbon content from the amount of carbon dioxide.*

2. The determination of the abrasion strength coefficient is carried out in accordance with GOST 16188–70. The method is based on the mechanical abrasion of a weighed portion of the zeolite sample, which is subjected to compression by a steel rod inside a rotating drum. By comparing the sample weight before and after the test, the percentage of the remaining non-dispersed fraction is determined, which characterizes the mechanical strength of the zeolite specimens.

3. The crushing strength of zeolite granules is determined using either a hydraulic or a mechanical press. The device represents a modified laboratory oil press equipped with a piston having a diameter of 58 mm. Compression and subsequent fracture of the granules occur between the piston and the pressing rod.

To measure the load applied to the granules, a standard precision manometer (class 0.2) with a pressure range up to 4 kg/cm² is mounted on the press’s pressure line. A sensor can also be connected to the manometer fitting to record the crushing force on a moving chart or tape.

According to this method, it is recommended to test 20–30 granules for each sample.

The specific crushing force, i.e., the load Рi (in kg per granule) corresponding to the destruction of a single granule, is calculated using the followingformula:

Рi =

*where:*

*Pim – pressure indicated on the manometer at the moment of granule failure, kg/sm²;*

*Sp – surface area of the piston, cm²;*

20 – number of granules tested.

4. The specific surface area can be determined using the volumetric method based on the volume of nitrogen adsorption corresponding to the formation of a monomolecular layer (aₘ) on the sample surface. This condition is typically achieved for porous materials when...

Р/Рs = 0,18 - 0,20.

The value of am (µmol/g) was calculated using the following equation:

аm =

*where:*

*m – mass of the sample, g;*

*P0 – initial nitrogen pressure, mm Hg;*

*P1 – residual nitrogen pressure after adsorption, mm Hg;*

*V1 – volume of the ampoule containing the sample, cm³;*

*V2 – remaining internal volume of the apparatus, cm³;*

*Tk – ambient (room) temperature, K;*

*Tₐ – temperature of liquid nitrogen, K.*

After calculating the value of am, the specific surface area of the sample is determined using the following equation:

*where: 0,09757 a constant factor equal to the product of Am; NA - Avogadro’s number: 6,023 ∙1023; Am - surface area occupied by a single nitrogen molecule, 16,2 · 10-20 m2.*

The total pore volume based on water absorption was determined in accordance with GOST 17219-71.

The adsorbent sample was dried, weighed, and then impregnated with water by boiling for 15 minutes, which ensures almost complete removal of air from the pores. Water from the spaces between the grains was removed by vacuum filtration at a residual pressure of 8 kPa (60 ± 5 mm Hg) for 3 minutes.

The increase in the sample mass determines the mass, and therefore the volume of water that filled the pores of the material with a diameter greater than 0.35 nm. From this, the pore volume and their fraction in the total material volume are calculated using the following formula:

sm3/g

*where: m1 and m2 - mass of the sample before and after water impregnation; - the density of water at the temperature of weighing the water-impregnated sample*

5. The bulk density of zeolites is determined according to the procedure described in GOST 16190-70.

The essence of the method lies in determining the mass of the sorbent occupying a defined volume under standardized compaction.

The crystallinity of fresh, spent, and regenerated zeolites was determined by X-ray diffraction using a DRON-2 diffractometer with a cobalt anticathode. The identification of diffraction peaks with interplanar spacings characteristic of the initial phases **Ca6(AlSiO4)12·30H2O** and **Na12 (AlSiO4)12 ·27H2O** was carried out according to **reference data.**

6. The adsorption characteristics of zeolites for H2O were determined [3,4] under the following conditions: adsorber diameter — 25 mm, zeolite bed height — 300 mm, volume of vapor–air mixture supplied for adsorption — 6 ± 0.25 dm³/min, moisture content in the mixture — 13–15 mg/dm³, adsorption temperature — 23 ± 3°C.

The dynamic activity (Ad) was taken as the amount of water vapor adsorbed by the zeolite (mg/sm³) up to the breakthrough point and was calculated using the following formula:

(6)

*where: V – volume of zeolite in the adsorber, cm³; m1 – mass of the zeolite before adsorption, g; m2 – mass of the zeolite after adsorption up to the breakthrough point, g.*

The breakthrough point was determined by the increase in the dew point temperature of the dehydrated vapor–air mixture, which was visually observed using a PTR-1 device by the clouding of a cooled polished plate, corresponding to the condensation temperature of water vapor.

The equilibrium activity (Ar) was calculated using the following formula:

(7)

where m3 – mass of the zeolite after complete saturation, g.

# RESULTS AND DISCUSSION

The obtained data on the physicochemical and adsorption properties of regenerated zeolite samples with diameters of 3.2 mm and 1.6 mm are presented in Tables 1.1 and 1.2.

The results demonstrated that the adsorption, mechanical, and textural characteristics (pore volume, specific surface area) comply with the standard specifications for CaA zeolites.

**TABLE 1.** Physicochemical and Adsorption Properties of Zeolite (d = 1.6 mm) Regenerated at 530 °C

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Name of the parameters | Regenerated | Fresh (Arcema) | Technical standards | Regenerated |
| Coke deposit content Expressed as carbon, wt % | resid. | resid. | resid. | resid. |
| Bulk density, g/cm³ | 0,8 | 0,77 | ˃0,7 | 0,8 |
| Dynamic activity for water vapor, mg/cm³ | 98 | 124 | ˃115 | 98 |
| Equilibrium activity for H₂O, mg/cm³ | 122 | 137 | ˃120 | 122 |
| Dew point, °C, °С | -50 | -61 | Not specified | -50 |
| Specific surface area by nitrogen, m²/g | 260 | 347 | Not regulated | 260 |
| Granule strength by generatrix length 5.5–6.0 mm, kg/granule | 9,76 | 10,65 | ˃1,5 | 9,76 |
| Abrasion strength, % min | - | - | ˂0,5 | - |
| Total porosity by water absorption, g/cm³ | 0,33 | 0,47 | ˃0,34 | 0,33 |

**TABLE 2.** Physicochemical and adsorption properties of zeolite (d = 3.2 mm) regenerated at 530 °C

|  |  |  |  |
| --- | --- | --- | --- |
| Name of parameters | Regenerated | Fresh (Arcema) | Technical standards |
| Coke deposit content expressed as carbon, wt % | resid. | resid. | resid. |
| Bulk density, g/cm³ | 0,78 | 0,71 | ˃0,7 |
| Dynamic activity for water vapor, mg/cm³ | 105 | 102 | ˃115 ford =1,6mm |
| Equilibrium activity for H₂O, mg/cm³ | 125 | 127 | ˃120 |
| Dew point, °C | -57 | -52 | Not specified |
| Specific Surface Area by Nitrogen, m²/g | 310 | 280 | Not regulated |
| Granule Strength by Generatrix Length 5.5–6.0 mm, kg/granule | 9,76 | 9,76 | ˃1,5 |
| Abrasion Strength, % min | - | - | ˂0,5 |
| Total Porosity by Water Absorption, g/cm³ | 0,35 | 0,36 | ˃0,34 |

The concentration of aluminum (Al) serves as an indicator of piston wear, the presence of chromium (Cr) reflects wear of the chromium-plated piston rings, and the presence of lead (Pb) corresponds to bearing wear.

# CONCLUSION

# The conducted studies showed that regeneration of zeolites at 530 °C preserves their main physicochemical properties. Thus, as a result of the conducted research, it was found that natural zeolites are acceptable in terms of adsorption capacity, mechanical strength, thermal stability and acid resistance in the processes of desulfurization of gases.After regeneration, zeolites can also be effectively used for natural gas desulfurization and drying processes.The adsorption activity, mechanical strength, and porosity of the regenerated samples meet the requirements of the regulatory standards. After regeneration, the zeolites can be effectively used for sulfur removal and natural gas dehydration processes.

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